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(54) IMPROVEMENTS IN OR RELATING TO FURNACES

(71) We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY, London, a British Authority, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an oxide resistor furnace element and to a furnace including such an element.

Furnaces having, as a heating element, a refractory metal oxide resistor are known and are usually referred to as "oxide resistor furnaces". Such furnaces are particularly suitable for operation in oxidising atmospheres. Examples of resistors which have been used in such furnaces are zirconia yttria resistors and zirconia-calcia resistors.

An operational difficulty of such furnaces is caused by the negative temperature coefficient of resistivity of oxide resistor elements. To overcome this difficulty, a supplementary heating means is provided to raise the temperature of such an element to a temperature at which it conducts a significant heating current. In the specification of our U.K. Patent No. 1,049,390, we have described and claimed an oxide resistor furnace wherein a supplementary heating means is provided.

In view of the provision of a supplementary heating means, end connectors in series with the oxide resistor element are required in order to convey an electric current from a supply terminal which is at room temperature to the element which may, for example, be at a temperature in the region of 1200°C to 1500°C. Platinum, for example, has been used as an end-connector material, but has the disadvantages of tending to vaporise at elevated temperatures and of being expensive.

According to this invention in a first aspect, there is provided an oxide resistor furnace element made of a refractory metal oxide other than lanthanum strontium chromite and having one or more electrical end connectors made of lanthanum strontium chromite.

We have found that the use of lanthanum strontium chromite according to the invention substantially overcomes the above mentioned disadvantages of platinum.

We prefer that the lanthanum strontium chromite has the general formula (I)

$$La_{1-x}\ Sr_x\ Cr_{1+z}\ O_{3+3z/2+y} \qquad (I)$$

wherein x is from one to zero, z is finite and is less than one, and y is from 0.5 to zero.

Lanthanum strontium chromite of the general formula (I) is particularly useful as an end connector material in the furnace element and furnace of this invention since it is particularly stable under operating conditions of the element in a furnace, and is stable during and after exposure to moisture. We believe that this stability may be due to the presence of an excess of chromium, as represented by Z, which constitutes a 'bank' to obviate the tendency of the chromium level to fall below one atom of chromium per 'molecule' of the oxide by vaporisation during operation as an end connector.

A particularly preferred lanthanum strontium chromite of the general formula (I) is

$$La_{0.84}\ Sr_{0.16}\ Cr_{1.05}\ O_{3.075}$$

The end connectors of the furnace element of this invention may conveniently be made by pressing the lanthanum strontium chromite, in powdered form, into the required shape. We prefer to use isostatic pressing and also to use a binder, such as "Cranco" (Registered Trade Mark) binder, in admixture with the powdered lanthanum strontium chromite.

According to the invention in a second aspect, there is provided an oxide resistor furnace comprising a furnace element according to the first aspect of this invention and a supplementary heating means for the furnace element.

A lanthanum strontium chromite of the general formula (I), as defined herein, may be prepared by mixing decomposable compounds of lanthanum, strontium and chromium in proportions such that the relative proportions of lanthanum, strontium and chromium correspond to their relative pro-

portions in the general formula (I), and calcining the mixture to decompose the compounds and give a lanthanum strontium chromite of the general formula (I).

For example, the compounds may be mixed in the form of solutions of salts, such as nitrates, of lanthanum, strontium and chromium. A lanthanum strontium chromite of the general formula (I) may, however, be made by other methods known in the art for preparing mixed oxides.

The invention will now be particularly described, by way of example only, with reference to the drawing accompanying the provisional specification which is a sectional view of an oxide resistor furnace.

Referring to the drawing, a zirconia-yttria tubular resistor 1 is supported between two cylindrical end-connectors 2 and 3, each of which is made of lanthanum strontium chromite. The resistor 1 and the end connectors 2 and 3 are supported within a cylindrical fire-brick surround 4, which has an inner recess 5 carrying a cylindrical zirconia heat shield 6 surrounding the resistor 1. Each end connector 2 and 3 is in touching contact with a cylindrical copper contact 7 and 8, each of which is provided with water cooling means (not shown) and is connectable to an electric power source. The resistor 1, the end connectors 2 and 3, and the copper contacts 7 and 8 are urged into contact by a spring (not shown).

Positioned within the resistor 1 is a pre-heater 9 constituted by a cylindrical alumina tube 10 having a "Nichrome" (Registered Trade Mark) alloy heating coil 11 mounted therein. The pre-heater 9 is retractably mounted so that it may be removed from within the resistor 1 by means of a winch (not shown).

The furnace is also provided with support members 12, 13, 14 and 15 and an outer case 16.

The gaps shown between the resistor 1 and each end-connector 2 and 3, between the end-connector 2 and contact 7, and between the end-connector 3 and contact 8 are not present in the final furnace but are merely shown in the drawing to enable the various components to be distinguished.

In operation, the resistor 1 is raised to a temperature at which it begins to conduct appreciable heating current by passing a current of 8 amps through the heating coil 11 of the pre-heater 9. Once the resistor 1 begins to conduct, i.e., at temperatures around 1130° as measured by a thermocouple (not shown), the pre-heater 9 is removed from within the resistor 1 by means of the winch (not shown). A current of 25 amps is passed through the resistor 1 via the copper contacts 7 and 8 and the end connectors 2 and 3. The resistor 1 is then allowed to increase in temperature of its own accord. The copper contacts 7 and 8 are maintained at ambient temperature by the water cooling means (not shown).

We found that the end-connectors 2 and 3 remained stable even after repeated use. In certain cases, they can form a sinter-contact with the material of the resistor 1; this can be readily dismantled on cooling, if it is so desired.

The contacts 7 and 8 may be made of materials other than copper, for example, they may be made of a high temperature alloy such as "Nimonic" (Registered Trade Mark) alloy which is an alloy of nickel and chromium containing, for example, 80% by weight of Ni and 20% by weight of Cr.

Also, the spring (not shown) for urging the resistor 1, the end connectors 2 and 3 and the contacts 7 and 8 in contact is not essential. Gravity may be sufficient. The heating coil 11 may be made of materials other than "Nichrome" (Registered Trade Mark) alloy, for example, it may be made of platinum or of silicon carbide.

The preparation of a lanthanum strontium chromite of the general formula (I), as defined herein, will now be exemplified as follows.

EXAMPLE

A mixed nitrate solution containing lanthanum, strontium and chrominum in the ratios required to make lanthanum strontium chromite was prepared by mixing 2404.7 g of a lanthanum nitrate solution containing 1.651 moles of lanthanum per kilo, 534.8 g of a strontium nitrate solution containing 1.414 moles per kilo and 2851.7 g of a chromium nitrate solution containing 1.740 moles of chromium per kilo to give a solution containing cations in the molar ratios La 0.84; Sr 0.16: Cr 1.05.

This nitrate solution was converted to a fine oxide powder, the particles composing it consisting of the oxides of lanthanum, strontium and chromium intimately mixed and partly reacted to chromite, by a high temperature spray reaction process as follows.

The solution was atomised, using a two fluid atomiser constructed in silica, into a tubular electrically heated reaction chamber mounted vertically. The reaction chamber consisted of a silica tube approximately 180 cm in length with an internal diameter of 10 cm. The wall of the reactor was maintained at 1000°C.

The droplets of solution, which had diameters in the range 10 μ to 100 μ, passed downwards through the reactor and were dried, decomposed to oxide particles, and partly reacted to chromite on exit from the base of the reactor at which point they had reached a maximum temperature of 700°C. Residence time in the reactor was of the order of a few seconds.

The product which was a pale greenish brown powder, was collected by disentraining

the oxide particles from the gas stream in a high efficiency cyclone which was connected to the outlet side of the reactor and operated by means of a compressed air ejector system. The particles composing the product tended to be hollow in nature and had diameters in the range 1 μ to 10 μ.

WHAT WE CLAIM IS:—

1. An oxide resistor furnace element made of a refractory metal oxide other than lanthanum strontium chromite and having one or more electrical end connectors made of lanthanum strontium chromite.

2. An oxide resistor furnace element according to claim 1, wherein the lanthanum strontium chromite has the general formula (I)

$$La_{1-x}\ Sr_x\ Cr_{1+z}\ O_{3+3z/2+y} \quad (I)$$

wherein x is from one to zero, z is finite and is less than one, and y is from 0.5 to zero.

3. An oxide resistor furnace element according to claim 2, wherein the lanthanum strontium chromite of the general formula (I) is

$$La_{0.84}\ Sr_{0.16}\ Cr_{1.05}\ O_{3.075}$$

4. An oxide resistor furnace element substantially as described herein with reference to and as shown in the drawing accompanying the provisional specification.

5. An oxide resistor furnace comprising an oxide resistor furnace element according to any of the preceding claims and a supplementary heating means for the furnace element.

6. An oxide resistor furnace substantially as described herein with reference to and as shown in the drawing accompanying the provisional specification.

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Agent for the Applicants.

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1451952 PROVISIONAL SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale